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Evaluation of toxic and genotoxic potential of a wet gas scrubber effluent obtained from wooden-based biomass furnaces: A case study in the red ceramic industry in southern Brazil

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A B S T R A C T

Red ceramic industry in southern Brazil commonly uses wood biomass as furnace fuel generating great amounts of gas emissions and ash. To avoid their impact on atmospheric environment, wet scrubbing is currently being applied in several plants. However, the water leachate formed could be potentially toxic and not managed as a common water-based effluent, since the resulting wastewater could carry many toxic compounds derived from wood pyrolysis. There is a lack of studies regarding this kind of effluent obtained specifically and strictly from wooden-based biomass furnaces. Therefore, we conducted an evaluation of toxic and genotoxic potentials of this particular type of wet gas scrubber effluent. Physical-chemical analysis showed high contents of several contaminants, including phenols, sulphates and ammoniacal nitrogen, as well as the total and suspended solids. The effluent cause significant toxicity towards microcrustacean *Artemia* sp. (LC_{50} = 34.4%) and *Daphnia magna* (Toxicity Factor = 6 on average) and to higher plants (*Lactuca sativa* L. and *Allium cepa* L.) with acute and sub-acute effects in several parameters. Besides, using plasmid DNA, significant damage was observed in concentrations 12.5% and higher. In cellular DNA, concentrations starting from 12.5% and 6.25% showed significant increase in Damage Index (DI) and Damage Frequency (DF), respectively. The results altogether suggest that the effluent components, such phenols, produced by wood combustion can be volatilized, water scrubbed, resulting in a toxic and genotoxic effluent which could contaminate the environment.

1. Introduction

The red ceramic industry is an important economic sector in the southern state of Santa Catarina, Brazil, based mainly on the production of clayey ceramic materials for use in the civil construction such as bricks, ceramic blocks and roofing tiles (Macedo et al., 2008). This production chain generates considerable amounts of solid and liquid residuals as well gas emissions that substantially impact the local environment. One crucial step of red ceramic production is firing the ceramic mass using wood or coal as the main energy inputs. This process produces significant loads of environmental contaminants such as CO, CO_2, NH_3, CH_4, nitrogen oxides (NOx), sulfur oxides (SOx), generic particulate matter and aerosols (Camara et al., 2015; Schwob et al., 2009; Souza et al., 2008).

To minimize this type of environmental impact, wet scrubbing has been used to control waste gas emissions of various industrial processes (Lanzerstorfer, 2000). In wet scrubbers, an absorbent (typically water) is dispersed into the flue gas. The specific gas phase is contacted with a liquid and is dissolved or diffused (scrubbed) into it. The interface between gas and liquid include liquid sheets, wetted walls, bubbles and even droplets (Fasihi et al., 2012). The simplest type of scrubber is the spray tower. In a spray tower, particulate-laden air passes into a chamber where it contacts a water spray produced by spray nozzles. The water spray can be generally directed counter to the gas flow or perpendicular to it and the droplets large enough to settle by gravity are collected at the bottom of the chamber (Woodard, 1998). Although almost all the amount of water used in this process continually recirculates into the system (refilling the spray nozzles) and, along the process, the sludge derived from the aggregation of heavy particulate matter accumulates within it and should be correctly disposed.

One recommended procedure is mixing this type of residue (sludge or wastewater) into the raw clay used by the plant, trapping this potentially hazard material within the final ceramic product itself becoming an inert material to the environment (Anderson, 2002;

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Cimdins et al., 2000). Since the ash composition of fly ash contains significant amounts of heavy metals and other organic and inorganic compounds which effectively presents toxic and genotoxic effects in several living organisms including humans (Chakraborty et al., 2009; Sherrard et al., 2015) the water leachate formed by gas scrubbing could also be potentially toxic. In fact, when coal fly ash is artificially leached, the resulting wastewater could carry many toxic compounds (Landsberger et al., 1995) that cause significant cellular damages in bacteria and even in higher plants (Chakraborty and Mukherjee, 2009). The management and disposal control of this type of residue is crucial to guarantee the environmental safety.

Bioassays are important tools for assessing the potential toxicity of environmental contaminants. To this end, a variety of techniques have been suggested using whole bioindicator organisms, isolated cells or macromolecules, organelles, enzyme systems to assess toxic, cytotoxic and genotoxic potentials (Kokkali and van Delft, 2014; Lanier et al., 2015; Lewis, 1995). Several studies have reported successful use of higher plants as a sensitive and rapid screening bioassay for assessing contamination of air, soil, surface water and groundwater, and residential and industrial effluents. In this context, *Allium cepa* L. (onion) and *Lactuca sativa* L. (lettuce) have been suggested as bioindicator organisms useful for ecotoxicological evaluation of contaminated environments (Bortolotto et al., 2009; Geremias et al., 2012; Rodrigues et al., 2013). *Allium cepa* as a bioindicator provides significant evidences of toxic and genotoxic effects of an environmental contaminant by several parameters including bioaccumulation of contaminants in roots, leaves and bulbs, inhibition of root growth, inhibition of seed germination, cytogenetic and mutagenic effects. The use of these plant in ecotoxicological tests has been suggested as it offers benefits including sensitivity, reproducibility, short response time, and the need for only a small volume of sample contaminant, in addition to low cost (Fiskesjo, 1985; Fiskesjö, 1988).

In a global scenario the inadequate management of the effluent produced by wet gas scrubbers in red ceramic industry could potentially contaminate the environment causing harmful effects to the living organisms. However there is a lack of evidences of this toxic and genotoxic potential regarding the use of wood and not coal as energy and then fly ash source. Therefore, this study aimed to evaluate the toxicity and genotoxicity of the water leachate from wet gas scrubber from red ceramic industry using physico-chemical parameters and bioassays.

2. Material and Methods

2.1. Collection and chemical analysis of the effluents

Four samples (5 L) of the effluent were collected from the water circulation system of one wet gas scrubber from a red ceramic plant in a city in the south of Santa Catarina state, Brazil. The sampling was performed every three months along one year totaling 4 samples (S1, S2, S3 and S4). These samples were stored in sealed polyethylene flasks and kept refrigerated until use. Unless noted, the data showed in following sections were expressed as mean ± SD of the four samples, to obtain a representative data of whole-year effluent sample.

The physical-chemical properties of each sample were determined at the Instituto de Pesquisas Ambientais e Tecnológicas (IPAT) of Universidade do Extremo Sul Catarinense (UNESC) using standard procedures. The analyzed parameters were: pH (by potentiometry), Chemical Oxygen Demand (COD, using closed reflux/colorimetric method), Biochemical Oxygen Demand of 5 days (BOD_5, by BOD_5 days test) and phenols (colorimetric method), Total Nitrogen (TN, by titration/Kjeldahl method), Total Suspended Solids (TSS) and Total Solids (TS) (both by gravimetric analysis) and sulphate content (by turbidimetric method). The results were compared to each other and to the maximum levels permitted under the Brazilian Environmental Legislations (CONAMA n° 430 from 13 May 2011, Art° 16 – Emission of effluents – to Total Nitrogen levels; and Environmental Legislation of Santa Catarina – Decree no. 14.250 from 5 June 1981, Art. 19 – Emission of liquid effluents – the other parameters).

2.2. Toxicity assays

2.2.1. Artemia sp. acute toxicity assay

The Artemia sp. acute toxicity assay was carried out according to Bortolotto et al. (2009) with minor modifications. A solution of salt water was prepared with synthetic sea salt (30 g L^{-1}) and used as the incubation medium for the cysts of *Artemia* sp. Young individuals (n = 10) were exposed in multi-well plates with 2 mL of effluent concentration (10–100%) and the negative control (0%), each in four replicates. All the dilutions had their salinity corrected to the same of the incubation medium with the direct addition of synthetic sea salt. After 24 h of exposure, the number of immobile organisms was counted with the mean lethal concentration (LC_{50}) being calculated by the Trimmed Spearman–Karber method (Hamilton et al., 1977).

2.2.2. D. magna acute toxicity assay

The *D. magna* acute toxicity assay was performed according to the Brazilian Standard Legislation guidelines (ABNT, 2004). Ten young organisms (24 h old) were exposed to 25 mL of the effluent at concentrations of 3.12%, 6.25%, 12.5%, 25%, 50% and 100%. The controls were prepared with the water used for dilution. After 48 h of exposure the number of immobile organisms was checked and noted, considering those that failed to move during 20 s of observation. At the end of the exposure the Toxicity Factor (TF which can be interpreted as the Lowest Ineffective Dilution, LID) was estimated, representing the highest effluent dilution that immobilizes 10% (or less) of organisms in the 48 h period.

2.2.3. A. cepa sub-chronic toxicity assay

The inhibition of root growth in *A. cepa* was observed as to examine the sub-chronic toxicity in effluent according to Fiskesjo (1988) with minor modifications from Bortolotto et al. (2009). Bulbs of *A. cepa* used in the experiments were obtained from the same well-known local commercial source. The bulbs (n = 6) were exposed to 50 mL of the effluent in concentrations of 100, 50 25% and 0% in falcon type tubes at room temperature for seven days in the dark. The 0% concentration stands to the negative control group using only commercial mineral water. The effluent solutions were replaced daily. At the end of the period of exposure, the length of the longest root from each bulb and total biomass of all roots were measured and compared to the control group (0%).

2.2.4. Lactuca sativa seed germination

Germination of L. *sativa* seeds was observed and performed according to Charles and et al. (2011) with minor modifications. Seeds (n = 10) were disposed on germination paper soaked with 2 mL of the effluent in a Petri dish (90 mm) at 22 °C in the dark. The treatments were arranged in a completely random design with three replications for each concentration (100, 75, 50, 25% and 0%). Percentage of germinated seeds and the growth of the seedling were determined 72 h after initial exposure. The germinated and growth in each treatment were compared to the control group (0%).

2.2.5. Microbiological tests

The effluents were submitted to Agar Diffusion Test as described by Silveira et al. (2011) to evaluate the bactericidal effects. The sensitivity of Gram-positive bacteria, *Staphilococus aureus*, and Gram-negative bacteria, *Klebsiela pneumoniae*, *Escherichia coli* and *Salmonela thyphimurium* to the effluent was analyzed using 100 μL of the brute effluents of each sample. The effluent samples were applied in a 10 mm hole in Petri dishes containing one bacteria specie together with a control group (H_2O) and incubated at 37 °C for 18 h (Silveira et al., 2011). After